

# Pulsed Laser Deposition of Carbon Nanomaterials

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## ABSTRACT

Nanostructured graphite and few-layer graphene (FLG) have been grown on copper and silicon substrates via pulsed laser deposition (PLD). This paper provides a parametric study of different experimental parameters and how they affect the resulting film growth in an effort to develop a better understanding of the underlying growth mechanisms of carbon nanostructures. The nanostructured order of the deposited films increases as the temperature of the substrate increases. The wavelength of the laser used affects the ablation of the carbon source, with lower wavelengths causing further breakdown of the carbon species. The carbon source and deposition pressure have interdependent effects which are explored, and the different substrates used affect the quality and morphology of the films.

**Keywords:** pulsed laser deposition, graphene

## 1 INTRODUCTION

Over the past several decades, nanomaterials have become the forefront of many research efforts. In particular, carbon has been fundamental for this development of novel nanostructures. The discovery of the C<sub>60</sub> fullerene in 1985 by Kroto et al. [1] was the first “zero-dimensional” material and the start of a nano revolution. This was followed by the one-dimensional carbon nanotube (CNT) discovery by Ijima [2]. Novoselov and Geim rounded out the dimensionality of carbon materials with the discovery of graphene in 2004 [3]. The allotropes of carbon, with the exception of diamond, can all be deconstructed into this basic building block structure of graphene. Since its discovery, graphene and other carbon and non-carbon nanomaterials have been extensively studied due to unique properties and widespread applications.

Graphene is a one atom thick, two-dimensional allotrope of carbon arranged in sp<sup>2</sup> bonded aromatic rings. It has become the area of focus for many different types of research groups due to its extraordinary properties. For example, graphene has exceptional electronic quality, which is evidenced by its large mobility [3], massless Dirac fermions [4], unique band structure, room temperature

quantum hall effect and ambipolar electric field effect [5]. In addition, graphene also displays interesting chemical, mechanical and optical properties, described elsewhere [6]. Due to these extraordinary properties of graphene, many applications across a huge number of fields have emerged, including graphene transistors, sensors, computer electronics and energy applications, to name a few [5,6].

Graphene can be fabricated using several different methods, each with its respective pros and cons. High electrical and structural quality graphene with micron sized lateral dimensions can be obtained by mechanical exfoliation, as initially displayed by Novoselov and Geim [3]. However, this method has limitations in the scale-up to large production levels, which has led to the development of other graphene growth methods. High quality graphene can be obtained by chemical vapor deposition (CVD), but with restrictions on how many layers can be grown. However, it utilizes high operating temperatures, typically above 1000°C [6]. In addition, epitaxial growth of graphene on SiC could provide a breakthrough for wafer-scale applications of epitaxial graphene. This method, which uses the thermal treatment of SiC to sublimate silicon atoms while the remaining carbon atoms rearrange and undergo graphitization, involves temperatures commonly exceeding 1300°C. While this method offers scale-up in production, the quality is not as good as exfoliated graphene and high temperatures limit economic viability [6].

Pulsed laser deposition, or PLD, is an extremely useful technique for creating thin films due to the flexibility of multiple parameters, non-equilibrium growth mechanisms and energetic evaporants. It is conceptually and experimentally simple, using a high powered, pulsed laser to vaporize material from a target and deposit it stoichiometrically onto a substrate material. This is done within a vacuum chamber, which can be evacuated or filled with reactive and non-reactive gases [7].

The growth of few layer graphene and other carbon nanostructures via pulsed laser deposition is not a new idea. However, growth conditions for individual experiments are not always consistent. This paper intends to provide information to reproducibly create films with desired properties based on various growth parameters.

## 2 EXPERIMENTAL DETAILS

Nanostructured carbon films were grown using PLD. The targets consisted of a pyrolytic graphite target (99.999%) and a carbon graphite target (99.999%) which rotate to avoid non-uniform material ablation. The laser used to irradiate the target is a Quanta Ray Nd:YAG laser operating at the second and fourth harmonics, 532 nm and 266 nm, respectively, with a 10 Hz repetition rate and a pulse duration of 7-10 ns. Laser fluence ranged from 3 to 8 J/cm<sup>2</sup>. Films were grown in a vacuum chamber evacuated to 10<sup>-6</sup> torr. The substrates used were n-type silicon <1 0 0> wafers and various copper foils, mounted parallel to the target at a distance of about 5 cm. The substrate was heated by a coiled resistance heater mounted under the substrate. The laser fluence was controlled by neutral density filters and by adjusting the laser spot size. The laser spot size was independently controlled by a focusing lens outside of the vacuum chamber.

Deposited carbon films were analyzed using a Raman spectrometer and a scanning electron microscope (SEM). Raman spectroscopy was used to characterize the samples. The samples were excited using an Ar ion laser (514 nm, 50 mW), focused to a spot of about 10 microns. Measurements were performed in a back-scattering geometry at room temperature using a Renishaw inVia Raman microscope. Sample morphology and thickness were analyzed using a Zeiss Sigma field emission scanning electron microscope.

## 3 RESULTS AND DISCUSSION

Raman spectroscopy has become the standard for reliable and non-destructive analysis of graphene [8]. Figures 1 and 2 show the Raman spectrum of carbon films grown on n-Si and copper substrates using 532 nm and 266 nm laser irradiation, respectively, at increasing substrate temperature, from room temperature up to 900°C. At room temperature (25°C), there is a single, broad peak centered near 1535 cm<sup>-1</sup>. This indicates an amorphous carbon structure with mostly disordered sp<sup>2</sup> bonding [9]. As the substrate temperature increases, the single broad peak separates into the D and G peak, at 1350 and 1600 cm<sup>-1</sup>, respectively. This indicates the formation of aromatic rings and the growth of nanocrystalline graphite as the temperature increases [9]. The disorder or D peak originates from small crystal size and unorganized carbon domains. This peak is due to zone-boundary phonons, which are not seen in defect-free graphite because the phonons do not satisfy the Raman fundamental selection rule [8]. It is also directly connected to the presence of aromatic rings [9]. The G peak originates from sp<sup>2</sup> bonded carbon atoms and is due to the doubly degenerate zone center E<sub>2g</sub> mode from in-plane vibrations [8]. The 2D or G' peak, shown in Figure 3 around 2700 cm<sup>-1</sup>, appears due to second order zone-boundary phonons and is a two-phonon double resonance Raman scattering process [10]. The 2D peak is sensitive to the number of layers of graphene and has been used to

effectively count the graphene layers when compared to the G peak [8]. These results are consistent with early Raman work by Cappelli et al. [11].

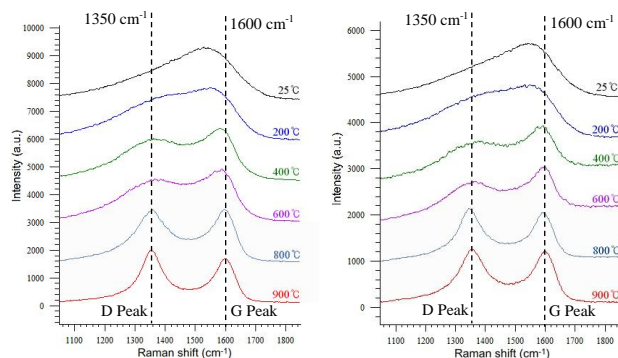


Figure 1: Raman spectra of carbon films grown using a 532 nm laser wavelength at different temperatures showing the evolution of the D and G peaks. Left is Si wafer substrate, right is copper foil substrate.

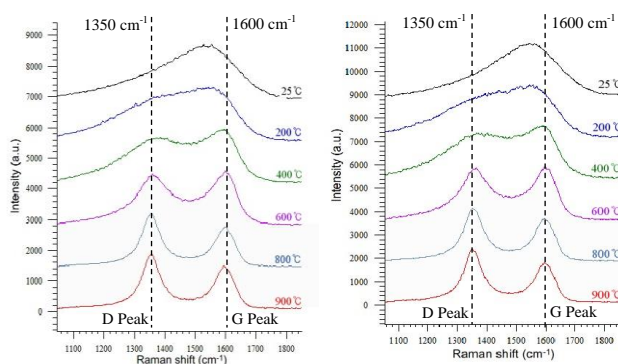


Figure 2: Raman spectra of carbon films grown using a 266 nm laser wavelength at different temperatures showing the evolution of the D and G peak. Left is Si wafer substrate, right is copper foil substrate.

By comparing Figures 1 and 2, it is evident that the growth mechanism is similar using different laser excitation energies and substrates. However, the carbon films grown using the 266 nm wavelength as the energy source begin to show more aromatic clustering at lower temperatures than films grown using the 532 nm wavelength. Between 400 and 600°C, the films grown with the 266 nm wavelength have shown more of separation of the D and G peaks, and a stronger D peak than the films grown using the 532 nm wavelength. The larger D peak can be explained by the presence of smaller domain sizes as the film approaches the nanocrystalline form of graphite earlier than the films grown using 532 nm irradiation. This is due to the laser interaction with the solid carbon target. Since the energy of the laser beam is larger when using 266 nm (4.66 eV) compared to 532 nm (2.33 eV), the resulting material ablated from the carbon target consist of smaller carbon species. With high enough laser flux and small enough wavelength, the carbon species can be controlled to be predominantly C<sub>1</sub><sup>+</sup> and C<sub>3</sub><sup>+</sup> ions [12]. As a result, the films

produced from the 266 nm wavelength consist of smaller carbon species, which lead to smaller nanocrystalline domains and a larger D peak at lower temperatures.

Figures 3 and 4 show the Raman spectra and peak fitting of FLG samples grown on copper substrates at 900°C using a laser fluence of 4 J/cm<sup>2</sup> and different laser wavelengths. By comparing these figures, it is evident that the FLG films grown using different laser wavelengths at high temperature are similar in structure. The only significant difference is the 2D/G ratio, which reveals that the film grown using 532 nm has slightly more layers of graphene than the film grown using 266 nm. With all other parameters being equal, this shows that the 532 nm laser irradiation ablated more material than the 266 nm laser irradiation.

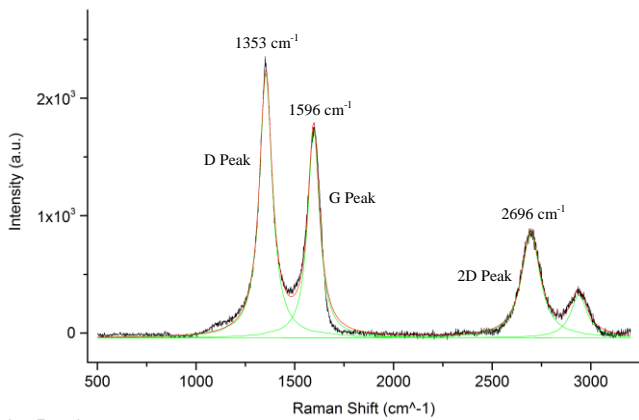


Figure 3: FLG film grown on a copper substrate using a 266 nm laser wavelength.

$$\frac{I(D)}{I(G)} = 1.26; \quad \frac{I(2D)}{I(G)} = 0.51$$

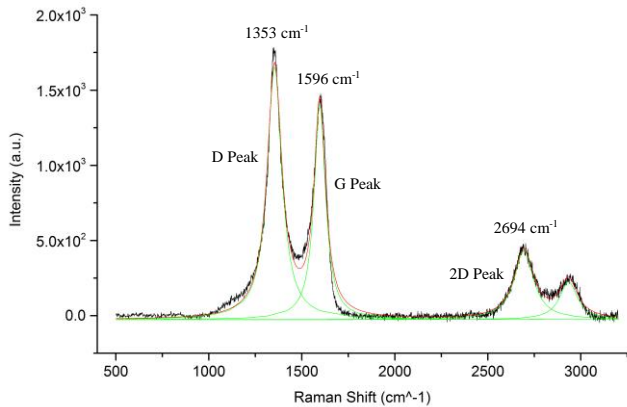


Figure 4: FLG film grown on a copper substrate using a 532 nm laser wavelength

$$\frac{I(D)}{I(G)} = 1.18; \quad \frac{I(2D)}{I(G)} = 0.32$$

When comparing the shape of the D and G peaks of the Raman spectra for different substrates in Figures 1 and 2, it

is evident that the shape of the D and G peak are unaffected by the type of substrate used. Further study of how the substrate material and morphology affects film growth was carried out by testing several different substrates for identical growth conditions. Figure 5 shows some of the different surface morphologies obtained by using different types of substrates, which have been pretreated in different ways prior to carbon film deposition.

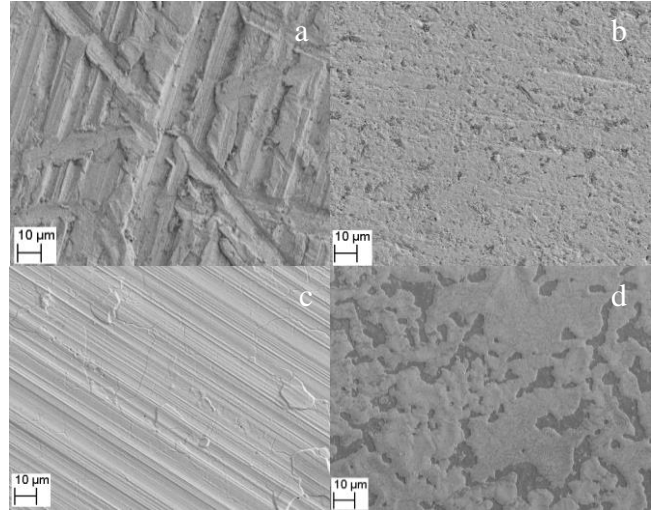


Figure 5: FESEM images of FLG on (a) copper sheet, (b) polished copper sheet, (c) copper foil and (d) electron-beam evaporated copper film.

Initial data that has been collected (Table 1) suggests that as the microstructure of the substrate material is improved, both the D/G and 2D/G ratios decrease. This was the case for the copper sheet substrates (0.675 mm thick) that could be polished. However, for the other substrates used, such as the copper foil and the evaporated copper film, no significant trends could be distinguished.

Target	Substrate	D/G Ratio	2D/G Ratio
HOPG	Virgin Cu	1.51	0.63
HOPG	Polished Cu	1.29	0.49
Graphite	Virgin Cu	1.60	0.65
Graphite	Polished Cu	1.36	0.58

Table 1: Ratios of the different Raman peaks of FLG films grown on different substrates from different sources.

The type of carbon source was explored to determine if and how it affected the resulting graphene films. Using pyrolytic graphite and carbon graphite target materials, it was determined that the source of carbon has little effect on the quality and domain of the graphene films when at high temperature and high vacuum. Table 1 shows the initial results of how the carbon source affects the resulting carbon film. However, it has been shown that when working in an argon atmosphere and at room temperature, the source of carbon makes a difference, and graphene films were unable to be made with compressed graphite targets as opposed to pyrolytic graphite targets [13]. This method of graphene

growth is more of an exfoliation technique than a layer growth via PLD due to the pressure at which the deposition occurs. The effect of pressure on the growth mechanism of carbon films is thus explored further.

Carbon films have been grown in an attempt to bridge the gap between laser ablation and exfoliation. Table 2 summarizes the initial results, which point to the source of carbon species being crucial for graphene growth at higher pressures. Films were grown at 1 torr argon at high and low temperatures using 532 nm laser wavelength to explore the mechanism of this high pressure growth. At low temperature the particulates are characterized by very large D peaks and the coverage consists only of the large particulates (1-10 microns). However, at high temperature there is widespread coverage of amorphous carbon on the substrate, similar to the spectrum in Figure 1 at 400°C. These films include particulates of extremely high quality FLG with a very small D peak, even from a graphite target. This shows a combination of laser ablation and laser exfoliation that could be extremely dependent on the deposition pressure, temperature and carbon source, and must be explored further to fully explain the phenomena.

Target	Temperature (°C)	D/G	2D/G
HOPG	20	1.54	0.41
HOPG	900	0.15	0.51
Graphite	20	0.95	0.12
Graphite	900	0.14	0.55

Table 2: Carbon nanostructures grown on a silicon wafer using 532 nm laser wavelength in 1 torr argon.

#### 4 CONCLUSION

Nanostructured graphite and few-layer graphene films have been grown on copper and silicon substrates via pulsed laser deposition. Experimental parameters are examined in detail to see how they affect film properties. We have found that as the temperature of the substrate increases, so does the order of the nanostructured films. As the laser energy increases, the ablated material from the carbon source become smaller since the increase in energy leads to further breakdown of the carbon species. Different substrates have different effects on the grown carbon films, with a general increase in quality as the surface morphology of the substrate increases. The source of the carbon species is still being investigated, but initial results reveal that under high vacuum, the source does not matter. However, at higher pressures, the carbon source could make a difference, and further pressure effects are currently being explored.

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